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(54) Title: METHOD FOR PREPARING A MIXED METAL OXIDE POWDER SUITABLE FOR THE PRODUCTION OF ELECTRICAL CAPACITORS

(57) Abstract

Method for preparing a mixed metal oxide powder suitable for the production of electrical capacitors, wherein a submicron barium titanate powder is suspended in a solution containing one or more dissolved metals from groups IIb, IVa, IVb, Va, Vb, VIb and VIIIb, the previously calcined barium titanate powder is impregnated with the solution, the solution is evaporated off and the powder thus obtained is pressed and then sintered. The method can be employed in the preparation of mixed metal oxide powders for the production of Standard X7R-compliant capacitors.

**Method for Preparing a Mixed Metal Oxide Powder  
Suitable for the Production of Electrical Capacitors**

This invention relates to a method for preparing mixed metal oxide powders suitable for the production of high-load capacitors, and to its use in producing a powder for the fabrication of capacitors which conform to the X7R standard (ANSI/EIA Standard 198-C-1983).

Mixed metal oxide compounds suitable for producing high-capacitive-load capacitors are traditionally prepared by mixing pre-ground metal oxide powders such as  $\text{BaTiO}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{MnO}_2$ ,  $\text{PbO}$ ,  $\text{ZnO}$  and  $\text{CoO}$  (US patent 4.499.521 in the name of North American PHILIPS Corp.).

Producing high-load multilayer capacitors, however, requires progressively finer powder so as to permit the creation of ever thinner dielectric layers needed for obtaining high capacitance values.

The powders obtained by established conventional methods generally display morphologies that are typical of ground powders, with average diameters greater than one  $\mu\text{m}$ , and therefore do not permit a further reduction of the thickness of the dielectric layer.

This invention is aimed at remedying the shortcomings of prior-art methods by introducing a method capable of producing submicron powders which are suitable for the fabrication of ultra-thin dielectric layers for high-load multilayer capacitors.

Specifically, the invention covers a method for preparing a mixed metal oxide powder suitable for the production of high-load capacitors, by employing a submicron barium titanate powder and one or several metal oxides from groups IIb, IVa, IVb, Va, Vb, VIIb and VIIIb. According to the invention, the previously calcinated barium titanate powder is suspended in a solution containing

dissolved metals, the barium titanate powder is impregnated with the solution, the solution is evaporated and the powder thus obtained is pressed and then sintered.

The term mixed metal oxide powder refers to a powder which contains the oxides of at least two different metals.

The high-load capacitors that can be produced by the method per this invention are multilayer capacitors where each layer consists of a dielectric material whose dielectric constant  $\epsilon$  at 25°C is greater than about 1800 and preferably greater than about 2000. This dielectric constant at 25°C may be very high, although in practice it rarely exceeds a value of about 5000.

The submicron barium titanate powder employed according to this invention can be obtained by any suitable method that produces barium titanate particles of a consistent grain size with an average diameter of less than one  $\mu\text{m}$ .

In a preferred implementation of this invention, the submicron barium titanate powder is prepared by coprecipitation arrived at by mixing an oxalic acid alcohol and titanium alcoholate solution with a barium hydroxide or acetate solution such as the one described in the Belgian patent application No. 9100836 in the name of SOLVAY & Cie (Société Anonyme).

Methanol is most advantageously used as the solvent of choice for the oxalic acid and titanium alcoholate.

In another, equally preferred implementation of this invention, the submicron barium titanate powder is prepared by the hydrolysis of a titanium alcoholate in the presence of a hydrated barium hydroxide and of a carboxylic acid containing more than 6 carbon atoms in its molecule, such as the one described in the French patent application No. 87.09116 in the name of SOLVAY & Cie (Société Anonyme).

In the latter implementation of this invention, the preferred carboxylic acid is selected from among the aliphatic acids with a linear carbonized chain. Excellent results have been obtained with oleic acid.

The metals of groups IIb, IVa, IVb, Va, Vb, VIIb and VIIIb of the periodic table of elements are preferably chosen from among silicon, niobium, bismuth, manganese and cobalt. It is imperative that at least one and preferably at least two of these metals be used. Excellent results have been obtained using three different metals out of the five preferred metals mentioned above. The best results have been obtained with a mixture of Nb, Bi and Mn.

According to the invention, the metals are dissolved in a solution. This is preferably an alcohol solution of one or several alcoholates and/or acetates of these metals. The preferred solvent is a possibly substituted aliphatic or alicyclic alcohol or a mixture of two or more of these miscible alcohols with one another in large proportions. The so-called "lower" saturated linear aliphatic alcohols, meaning those containing 1 to 6 carbon atoms in their hydrocarbonized chain, are well suited. The alcohols which contain 1 to 4 carbon atoms, such as the methylic, ethylic, n-propylic, isopropylic, n-butylic and isobutylic alcohols are the most suitable. Of these, methylic alcohol has yielded excellent results.

For the purpose of this invention the term metal alcoholate refers to a compound of the R-O-Me formula where Me is a metal atom and R represents a linear or ramified aromatic hydrocarbonized, alicyclic or aliphatic group, either saturated or containing one or several nonsaturations, either unsubstituted or containing one or several hydrocarbonized substituents, possibly including one or several heteroatoms in their principal chain. The metal alcoholates derived from a linear, saturated and possibly substituted aliphatic alcohol are preferred, examples being the

alcoholates derived from a lower aliphatic alcohol containing fewer than 5 carbon atoms, such as those where R is a methyl, ethyl, n-propyl, isopropyl, n-butyl or isobutyl group. A single metal alcoholate can be used equally well as a mixture of several alcoholates.

In a preferred form of implementation of the method according to this invention, the metallic alcohol solution is a mixture of the alcoholates or acetates of niobium, bismuth and manganese in a lower aliphatic alcohol. The best results have been obtained with a solution consisting of manganese acetate, bismuth acetate and a mixture of niobium ethylate and propylate in methanol.

In the method per this invention, the quantities of the metals to be dissolved are such that after the impregnation and evaporation of the solution the total metal content exclusive of Ti and Ba in the powder is greater than 0.5% by weight and preferably greater than 1%. It is desirable in any event to keep that content below 10% and preferably below 8%.

According to an interesting variation of the method per this invention, the metallic alcohol solution may advantageously contain one or several carboxylic acids. Aliphatic carboxylic acids such as the formic, acetic and propionic acids are well suited. Good results have been obtained with acetic acid especially in metallic methanol solutions.

According to the invention, the sintering of the powder is performed at a temperature sufficiently high for the barium titanate powder particles impregnated with metal acetates or alcoholates to form oxides of these metals along the perimeter of the particles. However, the temperature must not be so high as to inhibit the diffusion of these metal oxides toward the core of the particles. In practice, the sintering temperature is held between 1050°C and 1350°C.

This invention also relates to the use of the method disclosed for obtaining a powder to be

employed in the production of X7R-standard-compliant capacitors.

The X7R standard establishes a norm specifying an electrical capacitor whose dielectric constant does not vary more than 15% from either end of its rating at 25°C over an operating temperature range from -55°C to +125°C.

The following examples are given for the purpose of illustrating the invention without limiting its scope. Example 1R is given for comparison purposes. Examples 2 to 7 reflect implementations of this invention.

Example 1R: (not corresponding to the invention)

In a reactor containing a solvent consisting of a mixture of even amounts of methanol and isopropanol, a solution of Ti isopropylate and oleic acid is added to that solvent mixture in a manner as to arrive at a molar oleic acid/Ti ratio of 0.7 and a 0.0847 M Ti isopropylate solution. This is followed by the addition of a Nb alcoholate solution in the methanol previously prepared as described above, and a manganese acetate solution in methanol in an amount so controlled that the Nb/Ti molar ratio of the solution is equal to 0.02 and the Mn/Ti molar ratio is 0.002.

Thereupon, under agitation, a hydrated barium hydroxide is added to the even-part methanol/isopropanol mixture in an amount so controlled as to obtain a molar Ba/Ti ratio equal to 1.02. The resulting precipitate is then dried and calcined at up to 860°C.

The particles thus obtained are submicronic (90% have had a diameter of less than 1 µm), the average diameter being 0.5 µm.

The variations of the dielectric properties of the resulting powder as a function of temperature are shown in the graph of Fig. 1 which illustrates in the ordinate the evolvement of the dielectric constant  $\epsilon$  as a function of temperature (in degrees Centigrade) shown in the abscissa, measured with alternating current at a frequency of 1.5 kHz. Fig. 2 shows the relative variation, expressed in %, of the capacitance as a function of temperature (dC/C25°). The ordinates in Fig. 2 reflect the relative variation of the

capacitance ( $dC/C_{25^\circ}$ ) and are graduated in % while the abscissae, reflecting the temperature, are graduated in degrees Centigrade. It can be seen that the variations of the dielectric constant as a function of temperature are too great for the powder to be usable in the production of X7R-compliant capacitors.

Preparation of the Nb alcoholate solution:

1 liter of methanol and 34 g  $NbCl_5$  are placed in a glass balloon flask previously treated with compressed nitrogen. 68.5 ml propylene oxide is then added in an amount resulting in a molar propylene oxide/Nb ratio equal to 7.7, with the temperature controlled so as not to exceed  $32^\circ C$ , following which 1 ml of triethylamine is added.

The solution is allowed to react at room temperature for 2 hours and is then heated to  $40^\circ C$  over 2 hours.

Example 2: (according to the invention)

The following are successively placed in a glass balloon flask:

2.33 g	$BaTiO_3$ obtained by cohydrolysis in the presence of oleic acid and previously calcined at $850^\circ C$ over 2 hours;
30 ml	methanol;
2.05 ml	Nb alcoholate as a 0.122 M solution in methanol, prepared as in Example 1R;
25.0 ml	$Bi(CH_3COO)_3$ as a 0.01 M solution in a mixture of methanol and acetic acid; and
2.0 ml	$Mn(CH_3COO)_2$ as a 0.01 M solution in methanol.

This is followed by the evaporation of the solution at a reduced pressure and by the sintering of the powder obtained, at  $1175^\circ C$  over 1 hour. The molar ratio in the resulting powder is 0.025 for Nb/ $BaTiO_3$ , 0.025 for Bi/ $BaTiO_3$  and 0.002 for Mn/ $BaTiO_3$ .

The dielectric properties of the powder obtained as a function of temperature are shown in the graphs of Fig. 3 and 4, indicating the evolution of the dielectric constant as a function of temperature (in degrees Centigrade) and the relative variation of the capacitance (in %) as a

function of temperature, measured with alternating current at frequencies of 1.5 and 10 kHz. The abscissae and the ordinates in Fig. 3 represent the same magnitudes as in Fig. 1, those in Fig. 4 are the same as in Fig. 2. The solid line curves reflect the properties measured at 1.5 kHz, the broken line curves reflect the properties measured at 10 kHz. The maximum dielectric constant measured at 1.5 kHz is 2043 and corresponds to a temperature of 19°C, that measured at 10 kHz has a value of 2020 and corresponds to 102°C. At 25°C these dielectric constants measured 2042 (at 1.5 kHz) and 2003 (at 10 kHz).

It is evident that the capacitance variations as a function of temperature are minor and amount to less than 10% in the entire temperature range of interest. The powders obtained can thus be used in the production of X7R-standard-compliant capacitors.

The Bi acetate solution in the methanol and acetic acid mixture is prepared as follows: 1.42 g of  $\text{Bi}(\text{CH}_3\text{COO})_3$ , 17.5 ml acetic acid and 50 ml methanol are placed in an Erlenmeyer flask. After reflux heating of the mixture, 300 ml methanol is added under agitation.

Examples 3 to 6: (according to the invention)

Example 2 is reproduced with modification of the Nb, Bi and Mn content to where the powders have the following contents:

Example No.	Molar Ratio Nb/BaTiO <sub>3</sub>	Molar Ratio Bi/BaTiO <sub>3</sub>	Molar Ratio Mn/BaTiO <sub>3</sub>
3	0.025	0.020	0.002
4	0.025	0.030	0.002
5	0.025	0.040	0.002
6	0.025	0.025	0.005

The results obtained are shown in the graphs of Figures 5 to 12 which indicate the



evolution of the dielectric constant as a function of temperature (in degrees Centigrade) (Figures 5, 7, 9 and 11) and the relative variation of the capacitance as a function of temperature (Figures 6, 8, 10 and 12), measured with alternating current at frequencies of 1.5 and 10 kHz. The abscissae and ordinates in Figures 5, 7, 9 and 11 have the same significance as in Fig. 1, those in Figures 6, 8, 10 and 12 the same as in Fig. 2. The solid line curves represent the properties measured at 1.5 kHz, the broken line curves those measured at 10 kHz, with the exception of Fig. 11 and 12 which reflect measurements made at 100 kHz rather than 10 kHz. The maximum values and the values at 25°C of the dielectric constants measured are as follows:

Example No.	Figure No.	$\epsilon_{\max}$ 1.5 kHz	$\epsilon_{\max}$ 10 kHz	$\epsilon_{25^\circ\text{C}}$ 1.5 kHz	$\epsilon_{25^\circ\text{C}}$ 10 kHz
3	5	1902 (110°C)	1885 (113°C)	--	--
3	6	--	--	1703	1667
4	7	1972 (98°C)	1950 (100°C)	--	--
4	8	--	--	1914	1877
5	9	1730 (95°C)	1715 (98°C)	--	--
5	10	--	--	1605	1573
6	11	2091 (108°C)	2055 (111°C)	--	--
6	12	--	--	1922	1836*

(\*) = value measured at 100 kHz

As can be seen, the capacitance variations as a function of temperature are in all cases held between -15 and +15% over the entire temperature range of interest. All of the powders obtained can therefore be used in the production of capacitors compliant with the X7R standard.

**PATENT CLAIMS**

1. Method for preparing a mixed metal oxide powder suitable for producing high-load electrical capacitors, employing a submicron barium titanate powder and one or several metal oxides from groups IIb, IVa, IVb, Va, Vb, VIIb and VIIIb, characterized in that the previously calcined barium titanate powder is suspended in a solution containing the metals in a dissolved state, the barium titanate powder is impregnated with the solution, the solution is evaporated and the powder thus obtained is compressed and then sintered.
2. Method as in claim 1, characterized in that the barium titanate powder is obtained by coprecipitation as a result of the mixture of an oxalic-acid alcohol and titanium alcohol solution with a barium hydroxide or acetate solution.
3. Method as in claim 1, characterized in that the barium titanate powder is obtained by the hydrolysis of a titanium alcohol in the presence of a hydrated barium hydroxide and of a carboxylic acid containing more than 6 carbon atoms in the molecule.
4. Method as in claim 1, characterized in that the carboxylic acid is an oleic acid.
5. Method as in any one of the claims 1 to 4, characterized in that the metals are selected from among niobium, bismuth, manganese and cobalt.
6. Method as in any one of the claims 1 to 5, characterized in that the solution containing the dissolved metals is an alcohol solution of one or several alcoholates and/or acetates of the said metals.
7. Method as in claims 5 and 6, characterized in that the alcohol solution contains a mixture of the alcoholates or acetates of niobium, bismuth and manganese.

8. Method as in any one of the claims 1 to 7, characterized in that the alcohol solution is a methanol solution.
9. Method as in claim 8, characterized in that the methanol solution contains a carboxylic acid selected from among formic acid, acetic acid and propionic acid.
10. Use of the method per any one of the claims 1 to 9 in preparing mixed metal oxide powders for the production of capacitors compliant with the X7R standard.